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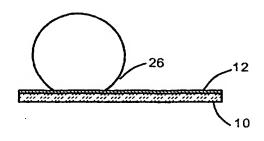
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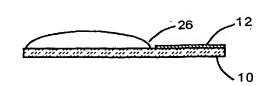
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[Continued on next page]

(54) Title: METHOD OF USING SHORT WAVELENGTH UV LIGHT TO SELECTIVELY REMOVE A COATING FROM A SUBSTRATE AND ARTICLE PRODUCED THEREBY





(57) Abstract: A method of selectively removing a functional organic coating from a substrate by exposure of the coating to short wavelength ultraviolet light. The UV light utilized in the invention preferably has a dominant wavelength of from 5 nm to 254 nm. The method is particularly useful for removing selected portions of a hydrophobic coating on a glass substrate for use as an automotive glazing.



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METHOD OF USING SHORT WAVELENGTH UV LIGHT TO SELECTIVELY REMOVE A COATING FROM A SUBSTRATE AND ARTICLE PRODUCED THEREBY

#### BACKGROUND

A method of removing a selected portion of a coating from a substrate is disclosed. More particularly, a method of removing a functional organic coating, for example, a coating having hydrophobic properties, with short wavelength ultraviolet (UV) light from a non-conductive substrate is disclosed.

Various types of coatings are often applied to nonconductive substrates such as glass to impart different
properties to the substrate. One such property which may
be imparted to a substrate, such as glass, by a coating,
is that of hydrophobicity. Hydrophobic coatings cause
water to bead readily and run off quickly. One
application where this property is useful is in the field
of vehicle glazing. Application of a hydrophobic coating
to a glazing in a vehicle, such as an automobile
windshield, backlight or sidelight can, by its properties,
cause water which comes into contact with the coating to
form into beads and quickly run off the glazing so as not
to obscure the outward vision of the occupants of the
vehicle. Particularly for the operator of the vehicle,
clearer vision is a safety benefit.

Much effort is expended in applying such hydrophobic coatings to a substrate, such as a vehicle glazing, to ensure that the coating strongly adheres to the substrate. It is, clearly, undesirable for the coating to begin to peel off the substrate, both from a functional and an aesthetic viewpoint.

It may be desirable, however, in some cases, to intentionally remove the coating from the substrate in selected areas. Such selective removal may be desirable, for example, if one wishes to adhere an item to the

substrate. In the case of vehicle glazings, it is often desirable to adhere one or more gaskets to portions of the peripheral edge of the glazing. It might also be desirable to adhere an item of hardware, such as a fastening device, a mounting device, or the like, in a particular location on the glazing.

Typically, hydrophobic coatings do not readily allow adhesive materials to adhere to them. So, in order to adhere a gasket or an item of hardware to the substrate, the coating must be removed, or it must have been selectively prevented from having been applied to the substrate in the first instance.

To date, efforts to solve this problem have been directed, primarily, to selectively preventing the coating from being applied to the substrate. One method of selectively preventing application of the coating is by masking the area where no coating is desired by applying an adhesive tape, a resist material, or the like, over those areas in which the coating is not desired.

While these methods are generally effective in preventing the application of the coating, they are uniformly costly, both in the cost of the masking materials and the labor necessary to apply them. Such masking also adds a lengthy step to the manufacturing process, thus greatly increasing cycle time when, for example, one is manufacturing high volume vehicle glazings.

Accordingly, it would be desirable to have a means to eliminate the need for costly operations, such as masking, and instead to have a quick and cost-efficient method to selectively remove an organic functional coating, such as a hydrophobic coating, from a non-conductive substrate, such as glass, and one which could be readily incorporated into a time-critical, automated manufacturing process.

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## SUMMARY OF THE INVENTION

It has been discovered that selective removal of such organic functional coatings can be efficiently accomplished by exposing the coated substrate to a source of short wavelength UV light. By short wavelength UV light is meant light having a dominant wavelength in the range of 5 nm to 254 nm. Preferably, the dominant wavelength of the UV light is from 100 nm to 200 nm. Most preferably, the dominant wavelength of the UV light is 172 nm.

More specifically, the present invention involves the selective removal of organic functional coatings having hydrophobic properties from the surface of a dielectric substrate, such as glass, in order to promote adhesion to that portion of the substrate from which the coating has been removed.

To selectively remove the organic functional coating from a large area of a dielectric substrate, for example, around the entire periphery of a vehicle glazing, or for the selective removal of such a coating from a substrate of large dimension, for example, a vehicle windshield or backlite, multiple sources of short wavelength UV light may be used.

Alternatively, a system of moving one or more sources of short wavelength UV light in a pre-determined pattern by electro-mechanical or opto-electro-mechanical means, for example, a robot arm, or a robot arm directed by an optical "vision system", may be utilized to selectively remove organic functional coatings.

The present invention also includes the article produced by the previously described method, particularly an automotive glazing from which an organic functional coating, such as a coating having hydrophobic properties, has been selectively removed.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

- Fig. 1 is a schematic layout of a short wavelength UV light removal system.
- Fig. 2 is a cross-sectional view of a dielectric substrate carrying an organic functional coating, a portion of which has been removed by exposure to short wavelength UV light.
- Fig. 3 is a cross-sectional view of a dielectric substrate as in Fig. 2 showing a fastening device adhered to the portion of the substrate from which the organic functional coating has been removed.
- Figs. 4 and 5 are cross-sectional views showing the difference in the water contact angle of a water droplet on a substrate where the organic functional coating is intact, and where a portion of the coating has been removed, respectively.
  - Figs. 6 and 7 are plan views showing examples of how organic functional coatings may be selectively removed utilizing the present invention.
- 20 Fig. 8 is a graphical representation of the change in water contact angle with time of exposure to short wavelength UV light.

#### DETAILED DESCRIPTION OF THE INVENTION

In order to accomplish the desired selective removal of organic functional coatings, the source of the short wavelength UV 14 light must be capable of emitting a beam of light which is primarily comprised of a single, dominant wavelength. Examples of such light sources are lasers, and excimer lamps. Manufacturers of suitable excimer lamps are, for example, Ushio Inc. and Heraeus Noblelight.

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Such light sources 14 should also be capable of being focused on precisely defined portions of the coated substrate 10 from which removal of the coating 12 is desired. For example, the above-mentioned lasers and excimer lamps have been demonstrated to remove coatings 12 to a precision of +/- 1 mm.

Further, for purposes of the present invention, it is important that the source of short wavelength UV 14 light be capable of removing the organic functional coating 12 within a relatively short exposure period, so that the coating removal operation may be incorporated into a timecritical manufacturing process, such as the high-volume production of automotive glazings. To this end, it has been determined that organic functional coatings 12 such as polysiloxanes, polyfluorosiloxanes and diamond-like carbon may be effectively removed by exposure to short wavelength UV light, having a dominant wavelength of about 172 nm, in a range of 5 to 120 seconds. It has also been determined that such exposure times may be longer or shorter depending on the "strength" of the light source By "strength" of the light source is meant the number of watts of power transmitted to the coated surface per unit area, for example, units per square centimeter. Further, it has been determined that the distance between the light source and the surface of the coating is important to removal efficiency. For the lamp tested, having a "strength" of 50 watts/cm<sup>2</sup>, optimal distance between the lamp and coating surface is 0 to 2 mm.

The effective removal of the organic functional coating 12 by exposure to the short wavelength UV light can be determined by measuring the water contact angle 26 both before and after the prescribed exposure period. The "water contact angle" 26 is the angle measured from the horizontal, between the base of a water droplet which is in contact with the coated substrate 10, 12 and the

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surface of the substrate, or the surface of the substrate from which the coating has been removed 20. The water contact angle 26 is, typically, measured by a visual enhancement system, for example, the system manufactured by AST Products, and a computer software package, for example, the package sold under the name VCA-2000 for Windows.

Utilizing the method of the subject invention, it has been found that the water contact angle 26 was reduced from greater than 100° to less than 30°, after exposure to the UV light, thus indicating that the coating 12 had been effectively removed from the desired area.

Once the organic functional coating 12 has been removed, the selected area may be made ready to have, for example, an elastomeric member or item of hardware attached to it. Preferably, an adhesion promoting primer 21, such as a silane primer, is applied to the selected area, after which an appropriate adhesive 22 is applied.

The elastomeric member may be, for example, a type of gasket. The adhesive 22 may be, any suitable adhesive, for example, cyanoacrylate, urethane, epoxy, acrylic, hot melt silicone, or pressure sensitive adhesives.

Table 1 shows the results of several experiments wherein the time of exposure of the organic functional coating 12 to the short wave UV light 14 was doubled in Tests 1-5 but then was increased by 20 seconds for Test 6. Column A shows the change in water contact angle with exposure time as the hydrophobic coating is affected by the short wavelength UV light. "Tin side" refers to the major surface of the glass substrate which was in contact with the molten tin of the float bath during the glass manufacturing process. The hydrophobic coating had been deposited on that major surface of the substrate, and so was the side treated. Column B shows results for treatment of the coating also on the tin side of the glass

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substrate with the short wavelength UV light source at a distance of 7.7 mm from the surface of the organic functional coating. The change in water contact angle is significantly less dramatic than Column A where the distance between the UV light source and the coated surface was between 0 and 2 mm. As can be seen, the water contact angle 26 decreased significantly in all cases after a 40-second exposure, and with respect to Column A, had decreased significantly after only a 20-second exposure. It is applicant's opinion that with respect to Column A, the water contact angle 26 of 10° ± 3° after a 60-second exposure shows that the organic functional coating has been substantially completely removed.

The water contact angle in these tests was measured by the methodology previously described herein.

Table 2 shows the results of various tests to demonstrate the effectiveness of removal of the organic functional coating 12 in relation to the strength of the adhesive bond created when standard adhesion promoting primers 21, compatible adhesives 22 and an attachment means 24 are applied to an area from which the coating has been removed 20 by exposure to short wavelength UV light. The time intervals of exposure carry over from the tests shown in Table 1. Columns A-C show the dynamic load necessary to break the adhesive bond, and the predominant failure mode(s).

More specifically, column A shows results of exposure where the organic functional coating was deposited over a previously applied, typically by silk-screening, layer of a mixture of powdered glass, color pigment, and optionally, a powdered electrically conductive metal, such as silver.

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Columns B and C shows the relative effectiveness of removal where the organic functional coating was deposited on the side of the glass in contact with the molten tin in the float bath (Column B), and where the organic functional coating had been deposited on the major surface of the glass which, in the glass manufacturing process, does not come into contact with the molten tin in the float bath, also known as the "air side" (Column C).

It can be seen that substantially improved adhesion was obtained in all cases after 40 seconds exposure to short wavelength UV light. Except for Column B, maximum adhesion occurred after 60 seconds exposure. After 60 seconds exposure, the adhesive bond was stronger than the glass substrate to which it was attached, as denoted by the predominant failure mode.

Table 1 - Effect of Short Wavelength UV Exposure on Water Contact Angle

	Treatment Time	(A) Contact Angle Tin Side	(B) Contact Angle 7.7mm shim
1	No treatment	111º ± 1º (	111° ± 1°
2	5 seconds	83° ± 26°	No change
3	10 seconds	67° ± 22°	No change
4	20 seconds	31º ± 12º	109° ± 2°
5	40 seconds	'19° ± 9°	· 80° ± 29°
6	60 seconds	10º ± 3º	100° ± 14°

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Table 2 - Effect of Short Wavelength UV Exposure on .

Adhesion to Glass Substrate or Glass Substrate to which a Frit has been Applied

		· (A)				
	Treatment Time	AT3513 frit				
	÷.	Shear Failure	Predominant			
		Load	Failure Mode(s)			
1	No treatment	301º ± 111 lbs.	PG			
2	5 seconds	323° ± 82·1bs.	PG			
3	10 seconds	453º ± 318 lbs.	PG			
4	20 seconds	435° ± 141 lbs.	PG, · LCFG			
5	40 seconds	659º ± 71 lbs.	PG, GB			
6	60 seconds	682° ± 58 lbs.	GB			

		(B)				
	Treatment Time	Tin Side				
	•	Shear Failure	Predominant .			
		Load Failure Mode(s				
1	No treatment	89º ± 38 lbs.	PG			
2	5 seconds	211º ± 103 lbs.	PG, GB			
3	10 seconds	539° ± 98 lbs.	PG, LCFG			
4	20 seconds	670° ± 100 lbs.	LCFG, PG, GB			
5	40 seconds	662° ± 113 lbs.	LCFG, GB, CF, LCFM, PG			
6	60 seconds	600° ± 226 lbs.	LCFG, GB, PG			

		- (C)				
	Treatment Time	Air Side				
		Shear Failure	Predominant			
	,	Load	Failure Mode(s)			
1	No treatment	54º ± 29 lbs.	PG ·			
2	5 seconds	335º ± 132 lbs.	LCFM, LCFG, PG			
3	10 seconds ·	557° ± 168 lbs.	LCFM, LCFG			
4	20 seconds	380º ± 159 lbs.	LCFM, PG			
5	40 seconds	408° ± 47 lbs.	LCFM			
6	60 seconds	594° ± 224 lbs.	LCFM, LCFG, GB			

Notes: Adhesive = Essex 73100/73005, Primer = 43518/43520A, Substrate 2 = E-coated steel, Bond area = 0.5 x 1"

Hydrophobic coating (NSG primer type) applied to glass using PNA pilot line
43518 primer wipe-on/wipe-off, 43520A = 30-minute cure at 70°F, 50% R.H., 24-hour (min) adhesive cure UV treatment at PNA using Ushio handheld light Samples tested in Instron at 10mm/min.

Sample assembly and testing by Andrea Schult

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Table 3 shows the effects of exposure on multiple samples of glass carrying a hydrophobic coating to short wavelength UV light on the water contact angle in order to determine the repeatability of efficiently removing the coating. The exposure times are the same as in Tables 1 and 2. It can be seen that the water contact angle changes erratically with short exposure time (5-10 secs.) but becomes more predictable with exposure time of 15-60 seconds (See Columns A-C). Coating removal has been, essentially and repeatably, achieved after exposure of 40 seconds.

Table 3 - Reproducibility of Effect of Exposure to 172nm
UV Lamp on Sidelights Coated Samples

		(2)	(5)			
l		(A).	(B)	(C)	· (D)	(E)
		Contact	Contact	Contact .	Average	Stdev
Sample	Time(s)	Angle 1	Angle 2	Angle 3		
1	5 `	107.3	77.6	72.7	85.87	18.72
. 2	. 10	75.2	91.8	63.4	76.80	14.27
3	15	45.6	35.2	40.8	40.53	5.21
4	. 20	32.7	26.4	26.4	28.50	3.64.
5	40 .	18.9	20.1	23 .	20.67	2.11
6	60 .	20.1	17.7	20.1	19.30	1.39

#### What is claimed is:

- 1. A method for removing a selected portion of a functional organic coating having hydrophobic properties from the surface of a substrate, comprising contacting said coating with short wavelength ultra-violet (UV) light.
- 2. The method of claim 1 wherein said substrate is glass.
  - 3. The method of claim 1, wherein the organic functional coating having hydrophobic properties comprises a polysiloxane.

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- 4. The method of claim 1 wherein a source of said short wavelength UV light is an excimer lamp.
- 5. The method of claim 1 wherein a source of said short wavelength UV light is a laser.
  - 6. The method of claim 1, wherein the dominant wavelength of said short wavelength UV light is from 5 nm to 254 nm.

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- 7. The method of claim 6, wherein the dominant wavelength of said short wavelength UV light is from 100 nm to 200 nm.
- 30 8. The method of claim 6, wherein the dominant wavelength of said short wavelength UV light is 172 nm.

9. The method of claim 1, wherein the water contact angle on said substrate carrying said coating prior to contacting said coating with said short wavelength UV light is greater than 1000.

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10. The method of claim 9 wherein the water contact angle on said substrate after said coating has been selectively removed by contact with said short wavelength UV light is less than 300 on those portions of said substrate from which said hydrophobic coating has been removed.

11. The method of claim 1 wherein an adhesion promoting primer compound is applied to a portion of said substrate from which said functional organic coating has been removed.

- 12. The method of claim 11 wherein an elastomeric member is bonded to said portion of said substrate to which the adhesion promoting primer has been applied.
  - 13. The method of claim 12 wherein said elastomeric member is a gasket.
- 25 14. The method of claim 1, wherein said selected portion of said functional organic coating is removed by said contacting in less than 120 seconds.
- 15. A method of removing a selected portion of an organic functional coating having hydrophobic properties from the surface of a glass substrate, comprising contacting said coating with UV light having a dominant wavelength between 5 nm and 254 nm.

- 16. A method of removing a selected portion of a hydrophobic coating from a major surface of a glass substrate by contacting said coating with short wavelength UV light, the source of said UV light being an excimer lamp, and the dominant wavelength of said UV light being between 100nm and 200 nm.
- 17. A substrate carrying a functional organic coating, said substrate having two major surfaces, said coating being applied to one of said two major surfaces, wherein a selected portion of said coated surface has been exposed to short wavelength UV light for a predetermined period of time in order to remove said selected portion of said coating from said substrate.
  - 18. The organic functional coating of claim 17 wherein said coating has hydrophobic properties.
- 20 19. An automotive glazing carrying a hydrophobic coating on one major surface thereof, wherein selected portions of said hydrophobic coating have been selectively removed from said glazing by contacting said selected portions of said coating with UV light having a dominant wavelength of between 5 nm and 254 nm.
- 20. The automotive glazing of claim 19 wherein the dominant wavelength of the UV light is between 100 nm and 200 nm.

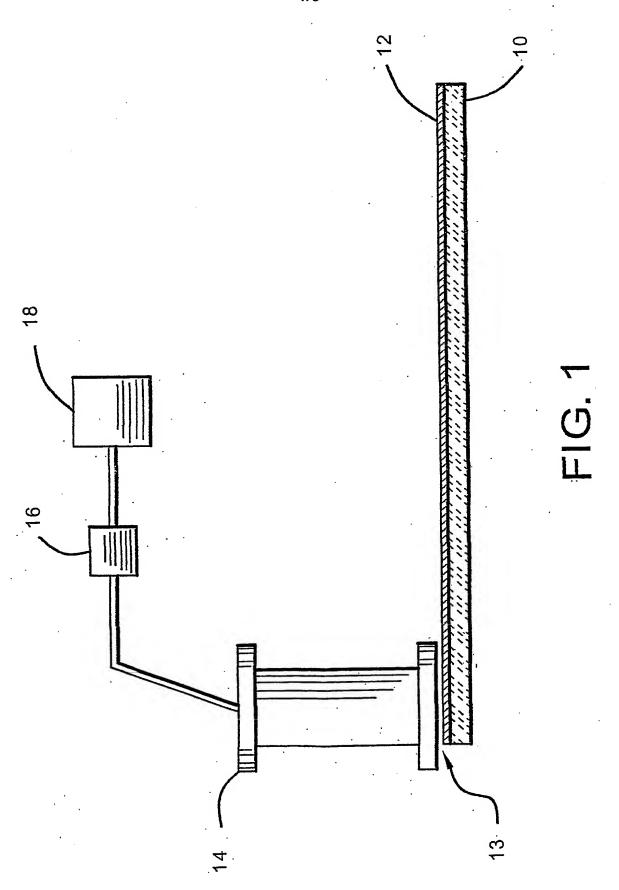
- 21. The automotive glazing of claim 19 wherein the dominant wavelength of the UV light is 172 nm.
- 22. A method of bonding hardware to a substrate provided with a functional organic coating, comprising: providing a substrate having a surface on which a functional organic coating has been applied; directing short wavelength UV light to a portion of said functional organic coating to thereby remove said portion of said functional organic coating from said substrate; applying an adhesion-promoting primer to said portions of said substrate from which said coating has been removed; applying an adhesive to that portion of the substrate to which the adhesion-promoting primer was previously applied; and bringing an elastomeric member or an item of hardware into bonding contact with said adhesive.

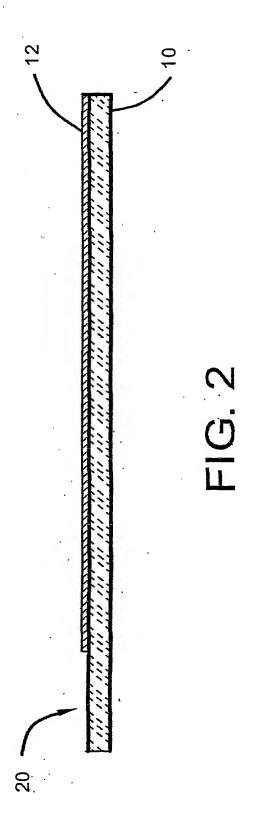
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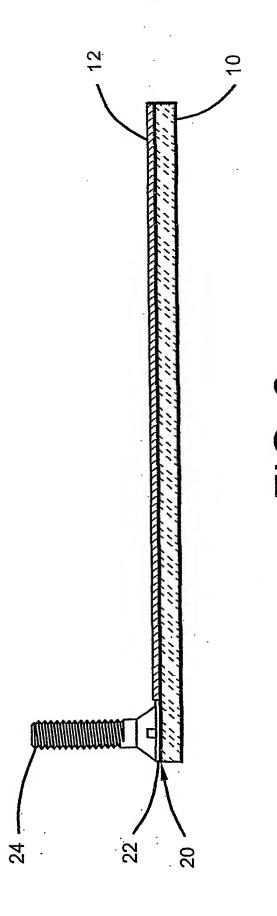
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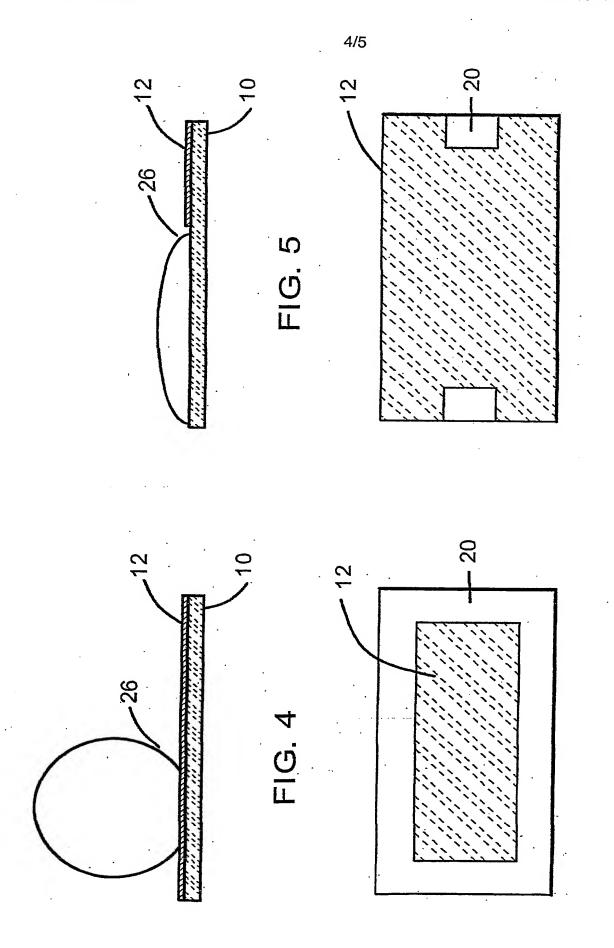








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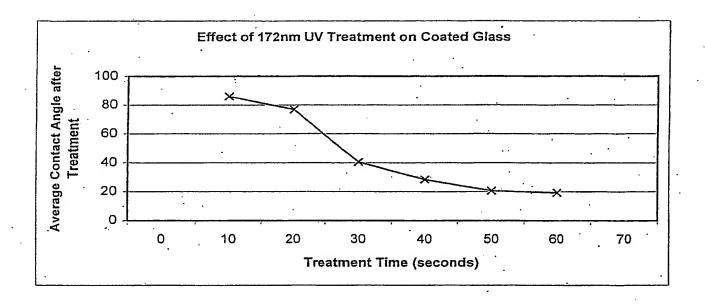


FIG. 8

#### INTERNATIONAL SEARCH REPORT

ernational Application No PCT/US 02/35404

a. classification of subject matter IPC 7 C03C17/00 C03C C03C17/22 C03C17/28 C03C17/30 C03C23/00 C03C17/34 According to International Patent Classification (IPC) or to both national classification and IPC Minimum documentation searched (classification system followed by classification symbols) CO3C Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, EMBASE, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Category 9 Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. X EP 0 577 187 A (PHILIPS ELECTRONICS NV) 1-10.5 January 1994 (1994-01-05) 14-17 column 3, line 57 -column 4, line 7 column 5, line 30 - line 41 column 5, line 52 - last line column 6, line 42 - line 45 example claims 5,7 X PATENT ABSTRACTS OF JAPAN 1-3. vol. 2000, no. 22, 9-13,17, 9 March 2001 (2001-03-09) 22 -& JP 2001 146439 A (CENTRAL GLASS CO LTD), 29 May 2001 (2001-05-29) abstract paragraph '0030! paragraph '0035! - paragraph '0045! X Further documents are listed in the continuation of box C. Х Patent family members are listed in annex. Special categories of cited documents: \*T\* later document published after the international filing date or priority date and not in conflict with the application but clted to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention 'E' earlier document but published on or after the international "X" document of particular relevance; the claimed Invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-O' document referring to an oral disclosure, use, exhibition or other means ments, such combination being obvious to a person skilled document published prior to the international filing date but later than the priority date claimed \*&" document member of the same patent family Date of the actual completion of the international search Date of malling of the international search report

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	ation) DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim No.
Category °	Citation of document, with Indication, where appropriate, of the relevant passages		nelevant to daim No.
(	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 12, 29 October 1999 (1999-10-29) JP 11 194202 A (NIKON CORP), 21 July 1999 (1999-07-21) abstract	1-8, 15-17	
	WO 01 19745 A (KOBAYASHI HIROAKI ;NIPPON SHEET GLASS CO LTD (JP); OGAWA HISASHI () 22 March 2001 (2001-03-22) the whole document		1-22
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

### INTERNATIONAL SEARCH REPORT

International application No. PCT/US 02/35404

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
Claims Nos.:     because they relate to subject matter not required to be searched by this Authority, namely:
2. X Claims Nos.: 18
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all
searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment
of any additional fee.
0 D Accelusario (III and III a
3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is
restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest  The additional search fees were accompanied by the applicant's protest.
No protest accompanied the payment of additional search fees.

Form DCT/ISA/210 (continuation of first sheet (1)) (July 1998)

#### FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 18

Present claim 18 relates to an extremely large number of possible products. In fact, the claim contains so many options, that a lack of clarity within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Furthermore the claim refers to an organic functional coating according to claim 17, whereas claim 17 refers to a substrate carrying the organic functional coating only. The subject matter of claim 18 is incompatible with claim 17 and yet is formulated to be dependent on this claim. This renders the extent of protection claimed obscure. Consequently only claim 1 to 17 and 19 to 22 have been searched.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

## INTERNATIONAL SEARCH REPORT

information on patent family members

PCT/US 02/35404

- 1	Dubliosilas	1		
	Publication date		Patent family member(s)	Publication · date
Α	05-01-1994	EP DE DE JP JP US	0577187 A1 69301009 D1 69301009 T2 3320504 B2 6088243 A 6316059 B1	05-01-1994 25-01-1996 04-07-1996 03-09-2002 29-03-1994 13-11-2001
Α	29-05-2001	NONE		
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Α	22-03-2001	EP WO	1218306 A1 0119745 A1	03-07-2002 22-03-2001
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Form PCT/ISA/210 (patent family annex) (July 1992)

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